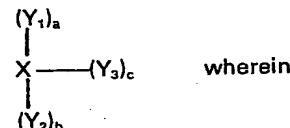

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(54) Durable, antistatic, soil release
agents and their application to
substrates

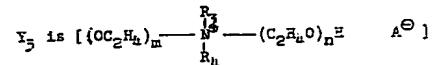
(57) A durable, antistatic soil release
agent which is resistant to yellowing on
the substrate has the formula



X is an aminoplast resin moiety
having 4 to 6 methylene groups, each of
which is attached to an amino nitrogen
atom and to Y₁, Y₂ or Y₃;

Y₁ is O(C₂H₄O)₅₋₂₀R₁ wherein R₁ is C₁₋₅
alkyl;

Y₂ is O(C₂H₄O)₅₋₈R₂ wherein R₂ is C₆₋₂₀
alkyl;



wherein R₃ is C₄₋₂₀ alkyl, C₄₋₂₀ alkenyl or
benzyl, R₄ is C₁₋₄ alkyl, A⁻ is an organic
or inorganic anion, each of m and n is at
least 1 and the sum of m and n is 12 to
100;

each of a and b is 0 to 2 and the sum
of a and b is 1 to 2;

c is 1 to 2;

the sum of a, b and c is 1 to 4;
said agent having a specified calculated
hydrophile-lipophile balance (HLB),
viscosity, electrical resistivity (initially
and after 10 washes) and soil release
rating on polyester fabric.

It is applied by

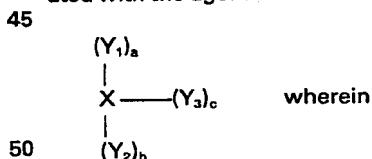
- diluting the agent,
- adding a metal or an ammonium
salt to achieve a cloud point of less than
100°C but greater than 25°C, and/or
adding sufficient polyacidic compound
having a second dissociation constant
of greater than 1 x 10⁻⁸ to achieve a pH
of 3.0 to 6.0,
- applying the diluted agent of step
(b) to the substrate, and
- drying and curing the agent on the
substrate.

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SPECIFICATION

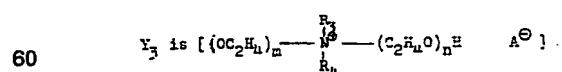
Application of durable, antistatic, soil release agents to substrates

- 5 This invention relates to a chemical composition which is useful for imparting durable antistatic and soil release characteristics to a wide variety of substrates, for example, textile fabrics, to a process for
 10 durably applying the composition to a substrate, and
 15 to substrate durably treated with the chemical composition.
- It is an object of this invention to provide a chemical composition which can be used to impart durable, antistatic, soil release and, to some extent, anti-soil redeposition characteristics to a substrate treated therewith. Another object is to provide a process by which the composition can be durably applied to the substrate. A further object is to provide a substrate which exhibits durable, antistatic, soil release and, to some extent, anti-soil redeposition properties. Still another object is to provide such a composition and process which are particularly useful in the textile trade.
- 20 Extensive prior art exists in the fields of antistatic agents and soil release agents. Such materials are used extensively to impart antistatic and soil release characteristics to substrates treated therewith, particularly textile materials, such as textile fabrics. A
 25 desirable feature of such agents is durability, that is, the ability of the agent to be retained on the substrate during subsequent handling or use thereof. For example, in the case of textile fabrics, such as clothing, it is desirable that any antistatic or soil release
 30 property imparted to the fabric be retained thereon through subsequent laundering operations. A need exists for a single substrate treating agent or composition which can impart durable, antistatic soil release properties to the substrate.
- 35 The invention resides in a durable antistatic soil release agent which is resistant to yellowing on the substrate treated therewith, to the method of applying the agent to the substrate, and to substrate treated with the agent which is of the formula



X is an aminoplast resin moiety having amino nitrogen atoms and 4 to 6 methylene groups, each of which methylene groups is attached to an amino nitrogen atom and to Y₁, Y₂ or Y₃;

50 Y₁ is O(C₂H₄O)₅₋₂₀R₁ wherein R₁ is C₁₋₅ alkyl;
 Y₂ is O(C₂H₄O)₅₋₂₀R₂ wherein R₂ is C₆₋₂₀ alkyl;



wherein R₃ is C₄₋₂₀ alkyl, C₄₋₂₀ alkenyl or benzyl, R₄ is C₁₋₄ alkyl, A[⊖] is an organic or inorganic anion, each of m and n is at least 1 and the sum of m and n is 12 to 100;

each of a and b is 0 to 2 and the sum of a and b is 0 to 2;

c is 1 to 2;

the sum of a, b and c is 1 to 4;

- 65 70 said agent having a calculated hydrophile - lipophile balance (HLB) of 14.5 to 18.0, a 20 weight% aqueous solution viscosity, as measured at 20°C on a Brookfield viscometer, of 250 to 16,000 cps (0.250 to 16.000 pascal seconds), an electrical resistivity (Keithley log R) on polyester fabric, at 20 ± 2% relative humidity (R.H.) and 23 ± 1°C, of no greater than 13.00 initially and no greater than 14.25 after 10 washes, and a soil release rating on polyester fabric of at least 3 initially. Preferably, in the above formula, Y₁ is
- 75 80 O(C₂H₄O)₁₀₋₁₆ and R₁ is CH₃; Y₂ is O(C₂H₄O)₁₅₋₃₀ and R₂ is C₁₃H₂₇; in Y₃, R₃ is C₈₋₁₈ alkyl, or C₈₋₁₂ alkyl to achieve good water wettability (drop absorption), R₄ is CH₃, A[⊖] is OSO₃CH₃ and m + n is 20 to 50; the HLB is 15.5 to 17.0; and the 20% aqueous viscosity is 85 2,000 to 8,000 cps (2.00 to 8.00 pascal seconds).

Although it will be described in greater detail hereinafter, the process of the invention resides in a process for applying the aforesaid agent to a substrate, which process comprises the steps:

- 90 95 (a) diluting the agent with a normally liquid medium to achieve the desired application liquid viscosity,
 (b) adding sufficient salt of a mono-, di- or trivalent metal or of an ammonium cation to achieve a cloud point, of the diluted agent of step (a), of less than 100°C but greater than 25°C, or adding sufficient polyacidic compound having a second dissociation constant of greater than 1 × 10⁻⁶ to achieve a pH, of the diluted agent of step (a), or 3.0 to 6.0, or adding 100 both said salt and said polyacidic compound to achieve said cloud point and pH,
 (c) applying the diluted agent of step (b) to the substrate to be treated so as to achieve the desired level of agent on the substrate,
 105 (d) drying and curing the agent on the substrate, and
 (e) recovering substrate which has been durably treated with the agent of the aforesaid formula.

Finally, the invention herein also resides in substrate which has been durably treated with the aforesaid agent.

The agent of the invention is prepared by conventional techniques by contacting, in appropriate amounts, under appropriate reaction conditions, 115 appropriate precursors of the aforesaid moieties X and Y₃ and the optional moieties Y₁ and Y₂.

Exemplary of X moiety precursors which can be used to produce the agent of the invention are the melamine methylol derivatives having 4 to 6 120 methylol groups, which methylol groups can be ether capped with, for example C₁₋₄ alkyl. The optional Y₁ and Y₂ moieties can be provided by the commonly available polyethylene oxides. For example, polyethylene glycol monoethers having 5 to 125 20 ethyleneoxy moieties and C₁₋₅ alkyl ether end groups are commercially available under the Carbowax® designation, thus providing a source of the Y₁ moiety. Similarly, the Y₂ moiety is provided by commercially available materials, such as those 130 designated Merpol®, which are polyethylene glycol

monoethers having 5 to 88 ethyleneoxy moieties and C₆-₂₀ alkyl ether end groups.

General procedure used to prepare Y₂ precursor

One mole of the appropriate C₆-C₂₀ alkyl alcohol is dried to ≥ 0.2 weight % water, either thermally under nitrogen purge or under reduced pressure (if the boiling point of the alcohol is high enough). About 0.5 part of sodium hydride (or a similar catalyst) is then added to the alcohol, with stirring, at 80-100°C, under a nitrogen atmosphere. After 15-60 minutes of agitation, the temperature is increased. When the alcohol temperature is about 140°C, the nitrogen purge is stopped and ethylene oxide is introduced. The temperature is allowed to reach about 155°C. The addition of ethylene oxide is continued at this temperature until a total of 5 to 88 moles (depending on the ethyleneoxide content desired) is added per mole of alcohol present. After addition and reaction of the ethylene oxide is complete, any sodium alcoholate formed (from the sodium hydride) is neutralized at about 70°C with an equivalent amount of acid, such as p-toluenesulfonic acid. The finished product, if it is not used immediately, can be stored in a sealed container until needed.

General procedure used to prepare Y₃ precursor

One mole of the appropriate n-alkylamine is heated under a nitrogen purge to at least 120°C, preferably within the range 185 to 230°C. The nitrogen purge is discontinued and ethylene oxide is introduced and reacted with the amine to produce N, N-bis - 2 - hydroxyethyl - n - alkyl amine according to the procedure of H. L. Sanders, J. B. Braunwarth, R. B. McConnell and R. A. Swenson, J. Am Oil Chem. Soc., 46 167 (1969). The lower molecular weight bis - 2 - hydroxyethyl - n - alkylamines are commercially available. About 1 part of 50-60 weight % sodium hydride in oil is then added to the one mole of the bis - 2 - hydroxyethyl - n - alkylamine under a nitrogen purge at 50-100°C. The mixture is heated with agitation under nitrogen to about 140°C. The nitrogen purge is discontinued, ethylene oxide is introduced and the reaction is run at 140-170°C, preferably at 155-165°C. Ethylene oxide addition is continued until the desired amount has reacted with the bis - 2 - hydroxyethyl - n - alkylamine. Then nitrogen purging is resumed while the product is cooled to about 80°C. An amount of acid, such as dry p-toluenesulfonic acid, equivalent to the 100% sodium hydride used is then added. The resultant tertiary polyethyleneoxy - n - alkylamine is quaternized by the following conventional procedure.

If a commercially available tertiary polyethyleneoxy - n - alkylamine is used, it should be dried 2-4 hours at 90-95°C with agitation under reduced pressure (30-50 mm of mercury; 3,999.7 to 6,666.1 pascal). To one mole of the aforesaid tertiary amine is slowly added, with agitation, 0.99-1.0 mole of dimethyl sulfate over a 1-4 hour period while the reaction mixture is kept at 50-60°C, after which the mixture is agitated for an additional 8-20 hours at 50-60°C. When the reaction is complete, the product can either be used directly in the subsequent condensation step or stored until such use.

General procedure used to prepare

agent of the invention

The agent of the invention can be prepared by the following general procedure. Although the procedure given below applies to the preparation of an agent of the aforesaid formula having Y₁, Y₂ and Y₃ moieties, it will be obvious to one skilled in the art that other agents of said formula wherein one or both of Y₁ and Y₂ are absent can similarly be prepared.

A mixture of one mole of the lower alkyl polyethyleneoxy alcohol (Y₁ precursor) and one mole of the higher alkyl polyethyleneoxy alcohol (Y₂ precursor) is dried and any peroxides therein are eliminated by heating, with agitation, at 170-190°C for 2 hours under reduced pressure (20-50 mm of mercury; 2,666.4 to 6,666.1 pascal). After cooling to 80-90°C and breaking the vacuum with a nitrogen purge, one mole of the quaternized polyethyleneoxy tertiary amine glycol (Y₃ precursor), one mole of predried hexakis (methoxymethyl) melamine (X precursor) (Cymel® 300) and 0.6 weight %, based on the total weight of the components used, of predried p-toluenesulfonic acid are added. With rapid nitrogen purging of the molten mass, the stirred mixture is heated at 90-95°C. The methanol and small amount of methylal that are evolved can be collected in cold receivers or traps. The total amount of methanol collected should be about three moles. The condensation is continued until the desired product viscosity is reached. An amount of tertiary amine, preferably having a boiling point above 120°C, for example, triethanolamine, which is 50 mole % greater than the molar amount of p-toluenesulfonic acid used is added immediately to the viscous mass to stop the reaction. The nitrogen flow rate and stirring rate are reduced while the amine neutralizes the acid at 85-95°C (10-20 minutes).

Aqueous dilution of condensate

The above 100% condensate can be stored as is or used directly. However, for most uses, such as the treatment of textile fabrics, it is diluted (by suspending or dispersing or by dissolving in a normally liquid medium) to a manageable viscosity, for example, the desired application liquid viscosity, so that it can be applied by conventional techniques, for example, by padding or exhaust. If the aforesaid 100% condensate has been stored at room temperature, it will be a solid and must be thawed at a temperature of at least 50°C, preferably under a nitrogen atmosphere. The condensate can be diluted with a normally liquid (at 25°C) medium until the desired (manageable) viscosity is achieved. The liquid medium preferably should be miscible with the agent of the invention and the salt and/or polyacidic compounds discussed hereinafter, nonreactive therewith at least up to about the cure temperature, and removable by volatilization at least by the cure temperature. Suitable liquid media include water, alcohols, ketones, esters, ethers and aromatic hydrocarbons. A convenient liquid medium for textile treating operations is water. Most of the description herein relates to the use of water as the normally liquid medium in connection with the utility of the agent of the invention as a durable, antistatic, soil release agent for textile fabrics. It will be readily

apparent to one skilled in the art that other substrates can be treated with the agent of the invention to achieve durable antistatic and soil release characteristics. For example, the agent of the invention can be used to treat textile fibers which may or may not subsequently be converted to fabric and to treat substrates which are flexible or nonflexible shaped structures of polymeric materials other than textile fibers and fabrics, for example, molded articles as well as extruded products, such as film and tubing.

If water is used as the normally liquid diluting medium, a weighed portion of the viscous condensate is added slowly to a rapidly stirred quantity of water (the addition of water to the condensate may yield a difficult - to - manage gel-like material). After the condensate dissolves, the mixture is made alkaline, for example, the pH is adjusted to 7.7-8.2, to minimize hydrolysis of the product on storage, by the addition of sodium bicarbonate. If desired, enough water can be added to bring the mass to, for example, a 20 weight % aqueous solution. Such a solution has a Brookfield viscosity of 250 to 16,000 cps (0.250 to 16.000 pascal seconds) at 20°C. In the treatment of fabrics, a more dilute aqueous solution is used, for example, less than 1 weight % in an exhaust application.

The agent of the invention has a calculated hydrophile-lipophile balance (HLB) of 14.5 to 18.0 and a 20 weight % aqueous solution viscosity, as measured on a Brookfield viscometer, of 250 to 16,000 cps (0.250 to 16.000 pascal seconds). In general, all other variables being maintained constant, the higher the viscosity, the better will be the durability achieved with the agent of the invention on the fabric being treated.

The Brookfield viscosity is determined by the American Society of Testing Materials Test Method D-1824, modified, with the modifications thereto being as follows:

- 40 1. Viscosities are measured at 25 ± 0.4°C.
2. Samples are bubble-free when viscosities are determined.
3. Viscosity is determined one to three times, on a given sample, at about the same time.
- 45 4. Viscosities are reported in centipoises (cps; pascal seconds).

The hydrophile-lipophile balance (HLB) system is the subject of numerous publications, for example, "Classification of Surface-Active Agents by HLB," W. C. Griffin, J. Soc. Cosmetic Chemists 1, 311 (1949); "Calculation of HLB Values of Non-ionic Surfactants," ibid. 5, 249 (1954); "The Atlas HLB System," Atlas Chemical Industries, Inc., Wilmington, Delaware, 4th printing, May, 1971; Proceedings 2nd Int. Congr. Sur. Act. 1, 426 (1957), Academic Press, New York, N.Y. HLB values reflect the hydrophilic content of the molecule. In accordance with the information available from the aforesaid publications, calculated HLB values are determined herein by means of the equation:

$$\frac{\text{sum of the molecular weights of all the hydrophilic moieties of the molecule}}{\text{molecular weight of the entire molecule}} \times 20 = \text{Calculated HLB}$$

65

The agent of this invention is particularly useful as a textile treating agent for fabrics of synthetic fibers, including woven, nonwoven and knit fabrics of either spun or filamentary type fibers. The fabrics can be of the blended or unblended fiber type. Fabrics treated with the agent exhibit good to excellent antistatic, soil release and, to some extent, anti-soil redeposition characteristics. Moreover, the agent does not substantially affect the hand of the fabric, and the agent appears to be non-toxic, it can be applied topically using pad or exhaust techniques, it is durably retained by the fabric after being applied thereto and it is resistant to yellowing on the fabric. Fabrics particularly suitable to treatment with the agent of this invention include those of polyester, polyamide, polyacrylic or acetate fibers. Qiana®, Nomex®, Dacron® and nylon taffeta fabrics, for example, can be usefully treated by means of this invention.

It is to be understood that the previous discussion of preparative procedures of the agent of the invention and the following examples (within the invention) and experiments (outside the invention) are intended merely as guidelines to enable one skilled in the art to practice the invention. Modifications of the preparative procedures disclosed herein will be readily apparent. It is to be further understood that the parameters set forth above for the agent of the invention are important to achieving the objects of the invention. Control of preparative conditions is important to achieving the requisite parameters of the agent and, although the details given above and hereinafter in the examples are believed to be adequate to practice the invention, ultimate determination of such practice usually is carried out by evaluating the agent, promptly after it is prepared, as to its various characteristics according to the procedures set forth below.

The fabric used in the evaluation of the agent of the invention is produced from commercially available Dacron® Polyester Fiber Type 56. The fabric is white, undyed 150/34 (denier/gauge) double-knit fabric. The fabric is scoured at 71°C for 20 minutes with 0.5 gram/litre (0.001 m³) of Merpol® SH nonionic detergent and 1 gram/litre (0.001 m³) of trisodium polyphosphate. After being rinsed well with water the fabric is dried.

The agent to be evaluated is padded onto the fabric so as to give an active ingredient level of 0.8 weight %, based on the weight of dry fabric. A typical pad bath includes the necessary amount of active ingredient, with the bath concentration being adjusted for wet-pickup of the fabric, 0.75 weight % of sodium sulfate, based on the total weight of the bath, and sufficient citric acid to achieve a pH of 4.0. Pad application can be carried out with a commercially available padder, such as a Spartan® II padder, using two passes and two nips. After padding, the fabric is dried and cured at 199°C in a forced hot air oven. Curing conditions may vary depending on the wet pick-up of the fabric. Generally, 60 to 75 seconds are adequate for curing at 199°C. A pin frame is used to hold the fabric.

The cured fabric is rinsed in Permutit® water to remove residual salts or acids and then dried, for

- example, in a commercially available Sears Roebuck dryer, at $71 \pm 5^\circ\text{C}$. The agent of the invention is tested for its antistatic characteristic on the fabric using the American Association of Textile Chemists and Colorists (AATCC) Test Method 76-1975 with slight modification as described below. Testing of fabric samples is carried out in a dry box at $20 \pm 2\%$ relative humidity and $23 \pm 1^\circ\text{C}$, the humidity being controlled by a commercially available Hygrometer Indicator Controller (Model 15-3252) with a Model 15-1810 sensing element. Testing equipment includes a Keithley Model 610C Electrometer in combination with a Keithley Model 240A High Voltage Supply and a Model 610S Resistivity Adapter.
- Further description of this test may be found in the AATCC Technical Manual under the aforesaid test method which is entitled "Electrical Resistivity of Fabrics." Testing of fabric samples is carried out initially (after rinsing) and then after five and ten home laundering/tumble dry cycles, commonly referred to as home wash/tumble dry (HWTD) cycles. The anti-static (A.S.) data appear in the accompanying tables under the heading "A.S." with the symbols "I, 5W, 10W" being used to indicate the antistatic characteristic initially and after five and ten washes (HWTD cycles), respectively. As indicated above, the agent of the invention must exhibit an electrical resistivity (Keithley Log R), a measure of the antistatic characteristic of the agent, on polyester fabric, at $20 \pm 2\%$ relative humidity and $23 \pm 1^\circ\text{C}$, of no greater than 13.00 initially and no greater than 14.25 after ten washes. For comparison, it may be noted that clean, untreated cotton broadcloth at about 20% relative humidity and about 23°C exhibits a Keithley Log R of 13.65 ± 0.05 . Untreated synthetic fabrics, in general, exhibit Keithley Log R values of 15.5 to 16.0.
- The home launderings are carried out, in general, according to AATCC Test Method 124. Equipment used includes a Sears Roebuck Kenmore automatic washer (Model 600) and a Sears Roebuck Kenmore automatic dryer (Model 600). This is the same dryer described above for drying the fabric samples which have been rinsed in Permutit® water. Test fabric specimens are cut to 20.3 cm squares and introduced into the washer along with "load fabric" (hemmed pieces of cotton sheeting; 97.4 cm squares) to give a total dry load of 1.81 kilograms. To the washer are added 28 grams of Tide® (commercially available) detergent. Washing is carried out under a normal wash cycle (12 minutes), at the high water level setting, using a hot water temperature of $60 \pm 3^\circ\text{C}$. The temperature of the rinse water used is $41 \pm 3^\circ\text{C}$. Soft water (hardness of no more than 5 ppm) is used. For hard water, Calgon® is added in an amount sufficient to reduce the hardness to a maximum of 5 ppm. Following washing and spin-drying the fabrics are dried in the dryer at a normal cycle time of 45 minutes, with the temperature dial being set on high to give a maximum stack temperature of $71 \pm 9^\circ\text{C}$. This cycle is repeated to achieve the desired number of home launderings.
- The soil release (S.R.) characteristic of the agent of this invention is determined, in general, by AATCC Test Method 130. The treated and cured fabric samples used in the soil release test are prepared in the same manner as those used in the antistatic performance test described above. The soil release test measures the ability of a fabric to release oily stains during home laundering and, as indicated above, the agent of this invention must exhibit a soil release rating on polyester fabric of at least 3 (initial), that is, before being subjected to the home laundering test. Data relative to this test are provided in the accompanying tables under the heading "S.R.", with data being included to show the soil release ratings initially (I) and after five (5W) and ten (10W) washes (HWTD cycles). Test specimens measuring 10 cm x 20 cm are conditioned for four hours at $21 \pm 1^\circ\text{C}$ and $65 \pm 2\%$ relative humidity prior to staining. A single flat thickness of test specimen is placed on AATCC Textile Blotting Paper on a smooth horizontal surface and five drops (each having a volume of about 0.2 ml; $0.2 \times 10^{-6} \text{ m}^3$) of a commercially available oil test liquid (60 weight% Nujol® and 40 weight% used piston engine automotive oil) are applied to the test specimen. The oil puddle (total volume, about 1 ml; $1 \times 10^{-6} \text{ m}^3$) which is formed is covered by a 7.6 cm x 7.6 cm piece of glassine paper and a 2.28 kilogram weight is placed on the paper. After 60 seconds the weight is removed and the glassine sheet is discarded. The oil-stained fabric specimen is then subjected to washing. Washing is carried out within 15 to 60 minutes of staining with such a number of test specimens that the total number of oil stains in the wash does not exceed thirty. Setting a maximum limit on the number of oil stains provides latitude in selecting the number of test specimens used in the event that it is desirable to place more than one oil stain on each test specimen. The aforesaid Kenmore Model 600 automatic washer is filled to the high water level with water at a temperature of $60 \pm 3^\circ\text{C}$. To the washer are added 140 ± 5 grams of AATCC Standard Detergent 124, or a known equivalent. Then the test specimens and cotton sheeting ballast, so as to make a total load of 1.8 ± 0.1 kilograms, are introduced. The washer is run through a normal wash cycle (12 minutes). Following completion of the spin-dry cycle, the specimens and ballast are placed in the aforesaid Kenmore Model 600 dryer. Drying is carried out at the high setting ($70 \pm 6^\circ\text{C}$), maximum stack temperature, for 45 ± 5 minutes. The dried test specimens are rated for residual stains within four hours after drying. Evaluation is made by comparing the residual stains in the test specimen with a standard soil release rating chart. Stains are rated to the nearest whole number from 1 to 5. The higher the number, the less is the residual stain.
- As stated above in the formula definition of the agent of this invention, R_3 preferably is C_{8-18} alkyl or, to achieve good water wettability (drop absorption), R_3 preferably is C_{8-12} alkyl. The drop absorption test used herein is, in general, based on AATCC Test Method 39. This test employs the same type of treated/cured fabric specimens described above. Fabric specimens are conditioned at $65 \pm 2\%$ relative humidity and $21 \pm 1^\circ\text{C}$ for at least four hours before testing. Each fabric test specimen is placed over the mouth of the cap of a 5.1-7.6 cm diameter jar. Water is dropped onto the surface of the fabric in a drop-wise fashion from a conventional eye dropper (each

drop having a volume of about 0.2 ml; $0.2 \times 10^{-6} \text{ m}^3$) held about 1 cm above the surface of the fabric. The time is measured, using a stop watch, from the moment that the first drop falls from the dropper until the wet area of the fabric loses its specular reflective power. This can best be observed by placing the fabric between the observer and a source of light, such as an outside window, at such an angle that the specular reflection of light from the surface of the flattened drop (as the drop hits the surface) can be plainly seen. As the drop is absorbed by the fabric, specular reflection of light ceases and a dull wet spot is formed on the fabric. High drop absorption times, for example, above 5 seconds, indicate poor wettability of the treated fabric.

Additional information on all of the aforesaid test procedures may be found in the AATCC Technical Manual.

Although the aforesaid testing procedures involve application of the agent of the invention to polyester fabric, optimum benefits from the agent of the invention are achieved using specialized techniques of application that are tailored to the type and characteristics of the fabric being treated. Details of these techniques are discussed below.

The application procedure for the agent of the invention is similar to procedures known in the trade for applying textile treating agents or fabric conditioners of the type disclosed herein. For example, procedures employed in the application of commercially available Zelcon® TGF Fabric Conditioner to polyester and certain polyester blend fabrics are similar to the procedure required to apply the agent of this invention to fabric materials. The results achieved with the agent of the invention are readily distinguishable from the results achieved with prior art textile treating agents such as Zelcon® TGF Fabric Conditioner. For example, whereas fabric treated with the latter, using conventional application conditions, does not exhibit durable (to home washes) antistatic behavior, fabric treated with the agent of the invention, using the application procedure described herein, retains its antistatic behavior through numerous home washes (HWTD cycles). This durability characteristic of the agent of the invention is believed to be related to the water-insolubilization which takes place during curing of the agent on the fabric.

As already indicated above, the agent of this invention can be applied by pad or exhaust procedures. In either procedure, the dilute aqueous condensate described hereinabove, for example, the weight % aqueous solution, must include certain acids and/or salts before it is applied to the fabric which is to be treated. The addition of an organic polyacidic compound and/or an at least divalent inorganic acid provides antistatic durability of the agent of the invention, when padded onto the fabric, through at least ten washes. The addition of a salt of a mono-, di- or trivalent metal or of an ammonium cation provides both soil release and antistatic durability of the agent, when either padded or exhausted onto the fabric, through at least ten washes. Preferably, for pad application, both the acid and the salt are present along with the agent of the invention to

achieve maximum effects. It has been found that, in exhaust application, the salt must be used alone. In other words, exhaust application cannot be carried out with acid along or with the combination of acid and salt. Regarding the polyacidic organic compound and the at least divalent inorganic acid, the second dissociation constant thereof must be greater than 1×10^{-6} . Examples of such materials include citric, oxalic, tartaric, succinic, glutaric and phosphoric acids. Boric acid, on the other hand, is unsatisfactory because the second dissociation constant is below the aforesaid minimum value. It has been found that low molecular weight polyacrylic acids also are useful herein. Although such materials are polyacidic, the various dissociation constants of the carboxy groups are not readily determinable because of the polymeric nature of the material. The operability of such an acid herein suggests that it meets the aforesaid requirement on second dissociation constant. Useful polyacrylic acids include those which are readily soluble in water. Such materials include those having molecular weights up to at least 5,000. In using the polyacidic compound, alone or in combination with the salt, the pH of the treating bath should be in the range 3.0 to 6.0, preferably 4.0 to 5.5. The function of the salt of a mono-, di- or trivalent metal or an ammonium salt, including an appropriate quaternary ammonium salt, appears to be related to its ability to lower the cloud point of the dilute aqueous solution of the agent of the invention below 100°C. The salt should have sufficient ionic strength to lower the cloud point below 100°C but it should not be such as to insolubilize the product at ambient temperature (25°C). Lowering of cloud point is determined using a 0.2 weight % aqueous solution of the agent. Examples of salts which may be employed herein alone or in combination with the organic polyacid include, but are not limited to, calcium, magnesium, zinc and sodium nitrates, the sodium phosphates, such as disodium hydrogen phosphate and trisodium phosphate, sodium, magnesium and calcium chlorides, sodium, magnesium, zinc and aluminum sulfates, sodium and ammonium oxalates, calcium acetate and diammonium citrate. Salt hydrates are equally useful. The use of the salt permits selective deposition of the agent of the invention during padding or exhaust; it decreases the mobility of the agent of the invention during the cure cycle and, thus, the agent is retained throughout the fabric (i.e., substantial amounts do not migrate); and it enhances the crosslinking which takes place during the drying/curing step as water is evaporated from the treated fabric. In general, it may be said that the cloud point is raised as the HLB increases but is lowered as the Brookfield viscosity is increased.

To exhaust the agent of the invention onto the fabric, the exhaust bath containing the agent, the appropriate salt, in an appropriate amount, and fabric material is heated to within about 5 to 10°C, for example, about 6°C, of the cloud point and held there until exhaust is complete. This is usually effected in no more than 5 to 10 minutes, for example, 6 minutes. The treated fabric is then removed from the exhaust bath, rinses or not rinsed (not rinsing is pre-

ferred), cooled, extracted of water (using conventional exhaustion techniques to remove excess water) and cured. Curing conditions will vary depending on the moisture content of the fabric, the higher the moisture content, the longer the time and/or the higher the temperature required. In general, for exhaust and pad applications, curing is carried out at 149 to 204°C. A preferred temperature range is 193 to 199°C. Curing at the preferred temperature conveniently can be carried out in less than one minute, for example, in 15 to 30 seconds, depending on moisture content and the weight of the fabric, when the agent of the invention is applied by exhaust techniques. For padding operations wherein moisture levels are higher, longer times usually are required, for examples, 60 to 75 seconds. Durability of the agent of the invention on the fabric requires careful control of curing conditions. Under-curing as well as over-curing will result in diminished durability of the agent. It is to be understood that curing conditions must be determined, for the most part, empirically.

For example, a hydrophilic fabric (that is, one retaining moisture readily) will require more rigorous curing conditions than a hydrophobic fabric. 25 Similarly, selection of salt and/or acid, and the amount thereof, are usually determined empirically. Evidence of the criticality of the curing conditions, in general, is provided in Table I. The table shows the antistatic and soil release behavior of the agent of the invention on the fabric initially and after five and ten washes. The agent used was that of Example 26 and the fabric to which the agent was applied was the same at that described above for test evaluation of the agent of the invention. The agent was applied 30 to the fabric by padding from a pad bath (of such concentration as to give 0.8 weight % of the agent on the fabric, dry weight) containing 0.75 weight % of sodium sulfate, based on the total weight of the bath, and citric acid to a pH of 4.0. Conditions of 35 drying/curing of the treated fabric are given in the table. As noted, in some instances, curing was preceded by a short drying step at a lower temperature.

TABLE I
Cure Conditions

Time (min)	Temp. (°C)	A.S.			S.R.		
		1	5W	10W	1	5W	10W
3	149	11.62	13.25	13.25	3	3	-
3	163	11.84	13.47	13.25	3	3	-
2	177	11.56	12.91	13.35	3	3	-
2	191	12.43	14.13	14.61	3	3	-
6	149	11.81	13.39	14.17	3	3	-
6	163	12.50	14.73	15.08	3	2	-
6	177	12.59	15.25	15.18	2	1	-
4	177	12.70	15.69	16.03	3	2	-
1	191	11.95	14.35	15.91	3	1	-
1	193	11.69	12.88	13.25	4	3	1
1	199	11.69	13.08	13.25	3	3	1
1	204	11.62	12.83	13.07	3	3	1
1	204	11.85	13.96	14.73	2	1	-
1.5	204	11.65	13.13	13.41	3	3	-
0.75	204	12.10	14.69	16.73	2	1	-
0.75	193	12.63	15.56	15.39	4	1	-
1	193	11.56	13.50	13.65	4	1	-
1.25	193	11.59	13.08	13.39	4	4	-
1.5	193	11.62	13.19	13.47	4	3	-
0.25*	193	11.24	12.81	13.08	3	4	-
0.5*	193	11.65	13.07	13.18	3	3	-
0.5*	193	12.43	13.37	13.56	3	3	-
0.75*	193	14.50	14.43	14.61	4	1	-
1*	193	13.24	14.95	15.53	4	3	-

*dried 3 minutes at 121°C.

Table II which follows includes data showing the effect of the addition of a salt and/or an acid to the agent of the invention in connection with the use of the agent in the pad (except as noted) treatment of fabric of the same type as that described above for test evaluation of the agent of the invention. The methods used to apply the agent were substantially 45 the same as those described above. The first column in Table II refers to the examples (hereinafter) in which the agent was made. Weight % concentrations shown are based on the total weight of the pad or exhaust bath.

TABLE II

	<i>Agent from Ex. No.</i>	<i>Salt</i>	<i>Conc'n. (wt %)</i>	<i>Acid</i>	<i>pH or (Conc'n.; wt %)</i>
5	3	Diammonium citrate	0.1	—	—
	3	"	0.2	—	—
	3	Diammonium citrate/ Sodium sulfate	0.1/ 0.75	—	—
10	3	"	0.2/ 0.75	—	—
15	8	—	—	Polyacrylic M.W. 2,000	(0.3%)
	8	—	—	Polyacrylic M.W. 5,000	(0.4%)
20	15	Calcium chloride	0.6	—	—
	15	Calcium chloride	0.4	Citric	4.0
	15	Sodium nitrate	0.3	Polyacrylic M.W. 5,000	5.5
25	17	Calcium acetate	0.6	Citric	4.0
	17	"	"	"	"
	17	"	0.93	"	"
	17	"	"	"	"
30	17	Calcium nitrate	0.75	"	"
	17	"	1.25	"	"
	24	Sodium nitrate	0.45	Citric	4.0
35	24	Zinc sulfate	1.0	"	"
	24	Zinc nitrate	1.0	"	"
40	24	Magnesium sulfate	0.5	"	"
	24	Magnesium nitrate	0.8	"	"
	26	—	—	—	—

TABLE II (Cont'd.)

Agent From Ex. No.	Dry/Cure			A.S. /	5W	10W	/	S.R. 5W	10W
	Temp. (°C)	Time (min.)	/						
5	3	193	1.0	13.06	14.61	15.20	4	2	1
	3	"	"	12.13	13.33	13.23	4	3	2
	3	"	"	13.02	14.43	14.65	4	5	2
	3	"	"	11.97	13.39	13.47	4	4	3
10	8	"	0.5	11.75	13.59	14.13	4	3	3
	8	"	"	11.65	13.43	13.61	4	4	3
	15	199	"	11.88	13.65	14.25	4	2	2
	15	193	1.0	11.84	13.47	13.95	5	4	2
15	15	"	"	11.65	13.03	13.11	5	5	3
	17	"	"	11.96	13.84	13.20	4	4	1
	17	"	"	11.69	13.19	13.23	4	4	2
	17	"	"	12.15	14.18	13.96	4	4	1
20	17	"	"	11.56	13.04	14.01	4	5	2
	17	"	"	12.37	13.56	13.17	4	5	5
	17	"	"	12.63	13.96	13.18	4	5	3
	24	"	"	11.93	13.00	13.61	3	5	5
25	24	"	"	12.31	14.11	14.18	3	4	5
	24	"	"	13.25	14.39	14.07	3	3	2
	24	"	"	12.11	13.39	13.73	3	5	5
	24	"	"	12.23	13.41	13.47	3	3	5
26	-	-	-	12.56	14.69	-	3	1	-

TABLE II (cont'd)

Agent from Ex. No.	Salt	Conc'n. (wt %)	Acid	pH or (Conc'n.; wt %)	
				0.75	-
30	Sodium sulfate	0.75	Tartaric	4.0	
			Citric	5.5	
			Glutaric	4.0	
			Succinic	4.0	
35	Calcium nitrate	-	-	-	-
			Tartaric	4.0	
			Citric	5.5	
			-	-	-
40	Na ₂ HPO ₄ · 7H ₂ O	1.0	-	-	-
		0.75	Tartaric	4.0	
		"	Citric	5.5	
		-	-	-	-
45	Na ₃ PO ₄ · 12H ₂ O	1.25	-	-	-
		0.5	-	-	-
		-	-	-	-
		-	-	-	-
50	Magnesium chloride · 6H ₂ O	0.4	-	-	-
			-	-	-
			-	-	-
			-	-	-
55	Sodium chloride	0.25	Oxalic	5.0	
			Citric	5.5	
			Succinic	4.0	
			Tartaric	4.0	
60	Sodium nitrate	-	"	4.5	
			"	5.0	
			"	5.5	
			Citric	4.0	
65	Sodium oxalate	-	"	4.5	
			"	5.0	
			"	5.5	
			"	5.5	

TABLE II (Cont'd.)

Agent from	Dry/Cure			A.S.	5W	10W	/	S.R.	5W	10W
	Ex. No.	Temp. (°C)	Time (min)							
5	26*	199	0.5	12.12	12.87	13.43	5	3	2	
	26	"	1.0	11.65	12.94	13.56	4	4	4	
	26	"	"	12.73	12.73	13.59	4	3	3	
	26	"	1.25	12.13	13.53	13.59	-	-	-	
10	26	"	"	12.12	13.61	15.01	-	-	-	
	26*	"	0.5	12.09	13.01	13.41	4	3	4	
	26*	"	"	11.96	13.03	13.61	5	3	4	
	26	"	1.0	12.27	13.25	14.24	3	4	3	
15	26	"	"	11.23	12.73	13.43	3	3	3	
	26*	193	0.5	12.06	13.13	13.35	4	3	4	
	26*	"	"	12.33	13.33	13.73	3	3	2	
	26**	"	"	12.56	13.33	14.04	4	3	3	
20	26**	"	"	12.37	13.59	14.13	4	3	3	
	26	199	1.25	12.14	13.65	13.95	3	3	2	
	26*	"	0.5	12.04	13.00	13.61	5	3	5	
	26	"	1.25	11.93	13.45	13.86	3	4	2	
25	26	"	"	11.59	13.39	13.21	4	-	-	
	26	"	"	12.19	13.87	13.73	-	-	-	
	26	"	1.0	11.65	12.85	13.39	3	1	-	
	26	"	"	11.83	13.00	13.61	3	1	-	
30	26	"	"	12.17	13.33	14.05	3	1	-	
	26	"	"	11.84	13.59	14.50	3	1	-	
	26	"	"	12.21	14.08	14.73	3	1	-	
	26	"	"	12.81	14.25	15.23	2	1	-	
35	26	"	"	11.96	13.18	13.96	3	1	-	
	26	"	"	11.97	13.53	14.21	3	1	-	
	26	"	"	11.69	13.24	13.73	3	1	-	

TABLE II (Cont'd.)

Agent from	Ex. No.	Salt	Conc'n. (wt %)	Acid	pH or (Conc'n.; wt %)	
					Citric	Oxalic
40	26	-	-	-	6.0	
	26	-	-	"	4.0	
	26	-	-	"	4.5	
	26	-	-	"	5.0	
	26	-	-	"	5.5	
45	26	-	-	"	6.0	
	26	-	-	Boric	(0.05%)	
	26	-	-	"	(0.1%)	
	26	-	-	"	(0.2%)	
	26	-	-	"	(0.4%)	
50	26	-	-	"	(0.6%)	
	26	-	-	85% H ₃ PO ₄	4.0	
	26	-	-	"	4.5	
	26	-	-	"	5.0	
	27	Calcium nitrate	0.75	-	-	
55	28	-	-	-	-	

TABLE II (Cont'd.)

Agent From	Ex. No.	Dry/Cure			A.S.	5W	10W	/	S.R. 5W	10W
		Temp. (°C)	Time (min)	/						
5	26	199	1.0	11.96	13.65	14.47	3	2	1	
	26	"	"	11.84	13.10	13.56	3	2+	-	
	26	"	"	12.01	13.13	13.69	3	2	-	
	26	"	"	11.56	12.84	13.35	3	1	-	
10	26	"	"	12.05	11.93	14.43	3	1	-	
	26	"	"	11.98	13.96	14.47	3	1	-	
	26	"	"	12.19	14.21	15.07	3	1	-	
	26	"	"	12.25	14.61	14.98	3	1	-	
	26	"	"	11.88	13.35	13.96	4	1	-	
15	26	"	"	13.11	14.59	15.73	3	1	-	
	26	"	"	13.21	15.21	15.95	3	1	-	
	26	"	1.25	11.85	13.13	13.93	4	4	-	
	26	"	"	12.19	13.33	14.25	4	4	-	
	26	"	"	12.11	13.22	13.90	4	4	-	
20	27	193	1.0	12.87	15.04	15.56	3-4	1	1	
	27	199	"	11.73	13.99	13.45	4	3	3	
	28	193	"	13.13	14.69	15.47	3	1	1	

*Applied to fabric by exhaust: 10 minutes at 66°C.

25 **Applied to fabric by exhaust: 10 minutes at 49°C.

Table III which follows includes data showing the
 30 effect of the addition of a salt and/or an acid to the
 agent of the invention in connection with the use of
 the agent in the treatment of fabrics other than that
 specified above in connection with the data included
 in Table II. In all cases, the agent of the invention

35 used was that of Example 26. Thus, the headings of
 Tables II and III are the same except that in the latter
 the Example No. heading has been replaced by the
 heading to designate the type of substrate fabric.

Application of the agent was carried out by padding
 40 as already described above.

TABLE III

	Fabric	Salt	Conc'n.	Acid	pH or (Conc'n.; wt %)
	Woven	calcium	(wt %)	Citric	4.0
5	Qiana®	nitrate	0.25		
	"	"	0.75	"	"
	"	sodium	0.25	"	"
10		sulfate			
	"	"	0.75	"	"
	"	Na ₂ HPO ₄ · 7H ₂ O	1.0	"	"
	"	"	0.5	"	"
15	Knit	sodium	0.75	-	-
	Qiana®	sulfate			
	"	"	0.75	Citric	4.0
	"	-	-	"	"
	White	sodium	0.75	"	"
	Qiana®	sulfate			
	"	"	"	"	"
20	Nomex®	-			
	"	sodium	0.5	Oxalic	"
		sulfate		Tartaric	"
	"	"	"	Citric	"
25	Red Nylon	calcium	0.75	"	"
	Taffeta	nitrate			
	"	"	0.25	"	"
	"	sodium	0.75	"	"
30		sulfate			
	"	"	0.25	"	"
	"	Na ₂ HPO ₄ · H ₂ O	1.0	"	"
	"	"	0.25	"	"
	Dull Spun	"	0.5	"	"
35	Acetate				
	Suiting	"	"	Tartaric	"
	"	-	-	Citric	"
	Acetate	sodium	0.5	"	"
40		sulfate			
	"	Na ₂ HPO ₄ · 7H ₂ O	"	"	"

TABLE III (Cont'd.)

	Fabric	Dry/Cure		A.S.	S.R.	5W	10W	
		Temp. (°C)	Time (min)					
5	Woven Qiana®	193	0.75	11.5	12.66	3	13.43	4
	"	"	"	11.89	13.03	3	14.19	3
	"	"	"	11.94	13.08	3	14.10	2
10	"	"	"	11.79	12.70	3	13.73	3
	"	"	"	12.25	13.50	3	14.65	2
	"	"	"	12.14	13.25	3	14.39	2
	Knit Qiana®	"	"	11.73	12.63	5	13.25	3
15	"	"	"	11.69	13.13	4	13.25	5
	"	"	"	12.08	12.90	3	13.47	4
	White Qiana®	182	1.0	12.08	13.53	5	14.19	3
	"	193	0.5	11.87	13.99	5	14.73	2
20	"	"	0.75	12.06	15.04	5	14.19	3
	Nomex®	188	1.0	13.28	13.88	3	14.25	—
	"	"	"	13.07	13.43	3	13.73	4
	"	"	"	13.02	13.73	3	14.32	—
	Red Nylon Taffeta	193	0.5	11.53	12.35	5	12.95	—
25	"	"	"	11.65	12.73	5	13.45	—
	"	"	"	12.03	12.96	5	13.65	—
	"	"	"	12.13	13.09	5	13.65	—
	"	"	"	12.09	13.45	5	14.24	—
30	"	"	"	12.07	13.15	5	13.23	—
	Dull Spun Acetate Suiting	182	0.75	12.73	13.25	2	13.73	—
	"	"	"	12.94	13.31	2	13.96	—
35	"	"	"	13.22	13.65	2	14.00	—
	Acetate	199	"	12.39	13.41	3	14.73	5
	"	182	"	12.45	13.53	2	14.25	—

TABLE III (Cont'd.)

	Fabric	Salt	Conc'n. (wt %)	Acid	pH or (Conc'n.; wt %)
40	Acrilan® Type 16	Sodium sulfate	"	"	"
45	Plain Weave	Na ₂ HPO ₄ · 7H ₂ O	"	Tartaric	"
	"	—	—	Citric	"
	Orlon®	Na ₂ HPO ₄ · 7H ₂ O	0.5	Tartaric	5.0
50	Type 75 Spun Yarn Plain Weave	—	—	Citric	4.0
	Arnel®	Na ₂ HPO ₄ · 7H ₂ O	0.5	Tartaric	4.0
55	Filament Tricot	—	—	Tartaric	5.0
	"	—	—	Citric	4.0
60	Spun Arnel® Plain Weave	Na ₂ HPO ₄ · 7H ₂ O	0.5	Tartaric	"
	"	sodium sulfate	"	Tartaric	"
65	"	—	—	"	"

TABLE III (Cont'd.)

	Fabric	Dry/Cure		A.S. 5W	10W	/	3	S.R.	
		Temp. (°C)	Time (min)					5W	10W
5	Acrilan®	182	0.75	11.87	12.27	13.24	3	2+	-
	Type 16								
	Plain Weave	"	"	12.25	13.00	13.88	3	2+	-
	"	"	"	11.97	12.63	13.61	3	3-	-
10	Orlon®	"	"	12.31	13.50	14.25	3	2	-
	Type 75								
	Spun Yarn								
	Plain Weave	"	"	12.56	14.05	14.35	2	2	-
15	Arnel®	"	"	12.70	13.59	-	3	3	-
	Filament								
	Tricot	"	"	12.73	13.84	-	3	3	-
	"	"	"	13.10	14.25	-	3	3	-
20	Spun	"	"	12.01	13.25	13.61	2	2	-
	Arnel®								
	Plain Weave	"	"	12.13	13.06	13.56	2	2	-
	"	"	"	11.98	12.70	13.50	2	2	-
25	"	"	"	12.17	13.35	13.98	2	2	-

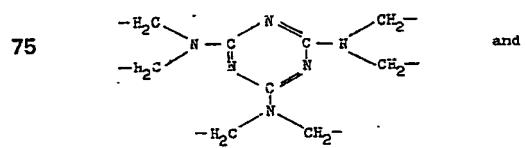
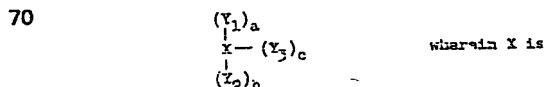
The amount of agent of the invention applied to the substrate being treated therewith will vary with the substrate and the nature and extent of the effect desired. For most textile applications, however, it has been found that 0.4 to 2.0 weight % of the agent on the fabric, based on the weight of dry fabric, imparts excellent, durable, antistatic soil release characteristics to the fabric. Generally, the preferred amount is 0.8 ± 0.1 weight %.

It also has been discovered in connection with this invention that the process of application of the agent of the invention to the substrate, as described herein, need not be followed in its entirety with respect to the treatment of certain substrates. More particularly, if the substrate is of sufficient polyacidic nature, the polyacidic compound described above need not, of necessity, be present in the treating bath. For example, fabrics made of fibers of acid-modified polymers, such as the commercially available acid-modified polyamides and acid-modified polyesters, can be usefully treated with the agent of the invention in the absence of the aforesaid requisite salt and/or polyacidic compound, that is, using only conventional aqueous treating bath ingredients, if sufficient acid-function is provided by the acid-modified polymer.

Examples 1 to 45

The following Examples 1 to 45 are intended to show various embodiments of the agent of the invention and the characteristics thereof. The techniques used in the examples to prepare the agents and to apply them to polyester fabric for evaluation are substantially the same as those already described above. More specifically with regard to the application of the agent to fabric, the agent included 0.75 weight %, based on the weight of bath, of sodium sulfate and sufficient citric acid to achieve a pH of 4.0. Dry/cure was affected in 1.0 to 1.25 minutes at 193 to 199°C. Data summarizing Exam-

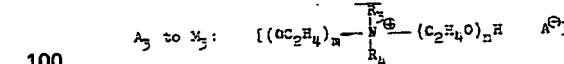
ples 1 to 45 are given in Table IV. All of the embodiments of the examples, except as noted below, are of the formula



80

Y_1 , Y_2 , Y_3 , a , b and c are as shown in the table. The various code designations shown in the table for Y_1 , Y_2 and Y_3 are defined as follows:

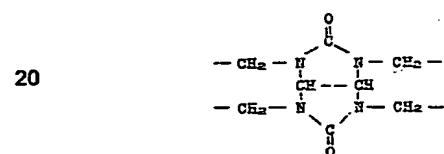
- 85 $A_1: O(C_2H_4O)_{12}CH_3$
 $A_2: O(C_2H_4O)_{15}$ straight chain $C_{13}H_{27}$
 $A_2': O(C_2H_4O)_{15}$ branched chain $C_{13}H_{27}$
 $B_1: O(C_2H_4O)_5$ straight chain $C_{13}H_{27}$
 $B_2': O(C_2H_4O)_5$ branched chain $C_{13}H_{27}$
 $C_1: O(C_2H_4O)_{25}$ straight chain $C_{13}H_{27}$
 $C_2': O(C_2H_4O)_{25}$ branched chain $C_{13}H_{27}$
 $D_1: O(C_2H_4O)_8$ straight chain $C_{13}H_{27}$
 $D_2': O(C_2H_4O)_8$ branched chain $C_{13}H_{27}$
 $E_1: O(C_2H_4O)_{45}$ straight chain $C_{13}H_{27}$
 $F_2: O(C_2H_4O)_{88}$ straight chain $C_{13}H_{27}$



wherein A^{\ominus} is OSO_3CH_3 and for A_3 to M_3 the following apply:

	<i>R</i> ₃	<i>R</i> ₄	<i>m + n</i>
A ₃ :	C ₁₈ H ₃₇	CH ₃	50
B ₃ :	C ₁₈ H ₃₇	CH ₃	16
C ₃ :	C ₈ H ₁₇	CH ₃	50
5 D ₃ :	C ₁₈ H ₃₅	CH ₃	24
E ₃ :	C ₈ H ₁₇	CH ₃	16
F ₃ :	C ₁₂ H ₂₅	CH ₃	42
G ₃ :	C ₄ H ₉	CH ₃	50
H ₃ :	benzyl	CH ₃	50
10 I ₃ :	C ₈ H ₁₇	CH ₃	24
J ₃ :	C ₄ H ₉	C ₄ H ₉	50
K ₃ :	C ₄ H ₉	CH ₃	12
L ₃ :	C ₁₂ H ₂₅	CH ₃	30
M ₃ :	C ₈ H ₁₇	CH ₃	100

15 In Example 44, X is



25

TABLE IV

	<i>Ex.</i> <i>No.</i>	(a)	<i>Y</i> ₁	(b)	<i>Y</i> ₂	(c)	<i>Y</i> ₃	<i>HLB</i>	<i>Viscosity</i> (pascal seconds)
30	1	0	—	0	—	1	A ₃	15.4	1.300
	2	1	A ₁	0	—	1	A ₃	16.1	1.300
	3	2	A ₁	0	—	1	A ₃	16.6	0.560
	4	0	—	2.3	A ₂	1	A ₃	15.6	8.280
35	5	0	—	2	A ₂	1	A ₃	14.5	0.580
	6	0	—	2	B ₂	2	A ₃	16.7	8.200
	7	0	—	1	C ₂	1	A ₃	16.1	2.000
	8	1	A ₁	1.2	A ₂	1	A ₃	16.1	0.610
	9	1	A ₁	1	A ₂	1	A ₃	16.1	4.600
40	10	1	A ₁	1	A ₂	1	A ₃	16.1	7.680
	11	1	A ₁	1	A ₂ '	1	A ₃	16.1	1.440
	12	1	A ₁	1	D ₂	1	A ₃	15.8	3.200
	13	1	A ₁	1	B ₂ '	1	A ₃	15.6	0.824
	14	1	A ₁	1	D ₂ '	1	A ₃	15.8	2.720
45	15	1	A ₁	1	C ₂	1	A ₃	16.4	8.780
	16	1	A ₁	1	E ₂	1	A ₃	17.0	6.180
	17	0.8	A ₁	1.2	A ₂	1	A ₃	16.0	7.300
	18	0.5	A ₁	1.5	A ₂	1	A ₃	15.8	5.900
	19	0.8	A ₁	1.2	C ₂	1	A ₃	16.4	10.800
50	20	0.8	A ₁	1.2	C ₂	1	A ₃	16.4	5.740
	21	0.5	A ₁	1.5	C ₂	1	A ₃	16.4	11.760
	22	0.5	A ₁	1.5	C ₂	1	A ₃	16.4	4.120
	23	1	A ₁	1	C ₂	1	A ₃	16.5	6.060
	24	1	A ₁	1	C ₂	1	A ₃	16.5	8.800
55	25	1	A ₁	1	C ₂	1	A ₃	16.5	8.960
	26	1	A ₁	1	C ₂	1	A ₃	16.5	8.200
	27	1	A ₁	1	C ₂	1	A ₃	16.5	2.400
	28	1	A ₁	1	C ₂	1	A ₃	16.5	2.400
	29	1	A ₁	1	C ₂	1	B ₃	14.9	4.450
60	30	1	A ₁	1	C ₂	1	C ₃	17.1	1.820
	31	1	A ₁	1	C ₂	1	C ₃	17.1	8.050
	32	1	A ₁	1	C ₂	1	D ₃	15.5	7.600

TABLE IV (Cont'd.)

	Ex. No.	/	A.S.		/	S.R.	
			5W	10W		5W	10W
5	1	11.96	12.07	12.95	3	3	2
	2	11.89	—	12.99	4	3	3
	3	11.98	14.25	13.47	4	4-5	5
	4	11.65	13.33	14.03	4	4	4
	5	12.59	13.85	14.13	4	4	3
10	6	11.69	13.30	13.53	4	3	2
	7	11.73	13.18	13.73	4	4	3
	8	11.59	13.19	13.08	4	5	3
	9	11.78	13.03	13.41	4	3	3
	10	11.73	13.08	13.59	3	2	2
15	11	11.77	12.99	13.98	4	4	3
	12	11.79	14.11	—	4	3	—
	13	11.62	12.90	13.61	4	3	2
	14	11.91	13.03	13.43	4	4	3
	15	11.69	12.95	13.43	4	4	3
20	16	12.17	13.37	13.56	4	4	3
	17	11.79	13.43	13.13	4	4	2
	18	11.73	13.19	13.22	4	4	3
	19	11.94	12.88	13.13	5	4	3
	20	12.04	13.13	13.47	4	4	3+
25	21	11.45	13.13	13.53	4	2	3
	22	11.97	13.18	13.25	3	4	3
	23	11.73	13.41	13.95	4	4	3
	24	11.84	13.14	13.43	3	4	3
	25	12.03	13.25	13.73	4	4	3
30	26	11.47	12.92	13.45	3	2	—
	27	11.41	12.73	13.61	3	3	2
	28	11.62	12.83	13.07	3	3	1
	29	12.28	13.20	13.49	3	2	2
	30	11.81	12.53	13.04	4	4	2
35	31	11.50	12.39	12.88	4	2	1
	32	11.62	13.19	12.95	4	4	3

TABLE IV (Cont'd.)

	<i>Ex. No.</i>	(a)	<i>Y₁</i>	(b)	<i>Y₂</i>	(c)	<i>Y₃</i>	<i>HLB</i>	<i>Viscosity (pascal seconds)</i>
5	33	1	A ₁	1	C ₂	1	E ₃	15.7	1.800
	34	1	A ₁	1	C ₂	1	F ₃	16.7	0.950
	35	1	A ₁	1	C ₂	1	F ₃	16.7	2.700
	36	1	A ₁	1	C ₂	1	G ₃	17.3	2.712
	37	1	A ₁	1	C ₂	1	H ₃	17.2	2.770
10	38	1	A ₁	1	C ₂	1	I ₃	16.2	12.700
	39	1	A ₁	1	C ₂	1	J ₃	17.2	6.200
	40	1	A ₁	1	C ₂	1	K ₃	15.8	1.000
	41	1	A ₁	1	C ₂	1	L ₃	16.3	2.750
	42	1	A ₁	1	B ₂	1	A ₃	15.6	0.420
15	43	1	A ₁	1	F ₂	1	A ₃	17.8	2.860
	44	1	A ₁	1	C ₂	1	A ₃	16.8	4.200
	45	1	A ₁	1	C ₂	1	A ₃	16.5	4.360
				<i>A.S.</i>				<i>S.R.</i>	
20	<i>Ex. No.</i>	/	5W	10W	/	5W	10W		
	33	11.95	13.11	13.98	5	4	4		
	34	11.30	12.59	12.73	3	1	1		
	35	11.29	12.59	12.70	3	2	1		
	36	12.14	13.02	14.20	4	4	2		
25	37	11.86	13.53	13.69	3	2	2		
	38	12.14	12.70	13.39	4	3	2		
	39	11.65	13.07	14.03	3	1	-		
	40	11.56	14.02	-	4	1	1		
	41	11.69	13.45	13.69	3	4	3		
30	42	11.69	13.33	13.43	4	3	3		
	43	12.23	13.92	13.98	3	-	-		
	44	11.85	13.37	13.95	3	-	-		
	45	11.65	13.39	13.53	3	-	-		

35 Example 46

The purpose of this example is to show the anti-soil redeposition characteristic of the agent of the invention. Unlike the other advantageous characteristics of the agent, there is no industry-accepted or standard test for measurement of soil redeposition. The test employed herein, in general, is the same as the aforesaid home laundering AATCC Test Method 124, using Table I, III Machine, except as noted below. The test is carried out using redeposition soil consisting of, on a weight basis:

Germantown Lamp Black	9.7 parts
Crisco®	29.1 parts
Nujol®	41.8 parts
50 Wheat starch (screened through a 100-mesh sieve, U.S. Sieve Series)	19.4 parts

Total parts: 100.0

55 The Crisco® and Nujol® are heated to 38°C and the lamp black and starch are added with stirring at this temperature until a homogeneous mixture is obtained. The redeposition soil is stored under refrigeration until used. The treated fabric samples, prepared as described above, are washed, along with the ballast load fabric. The redeposition soil is added along with the detergent (10 grams of soil are admixed with 50 grams of Tide® commercially available detergent; a paste is formed by admixing in the

presence of 100 ml ($0.1 \times 10^{-3} \text{ m}^3$) of 82-93°C water).

The soil is uniformly dispersed in the washing machine before the ballast and test samples are introduced. Washing is carried out under the normal

70 wash cycle (12 minutes) using a hot water temperature of $60 \pm 3^\circ\text{C}$. After the test samples are dried, as described hereinabove, they are compared with corresponding unsoiled fabric samples using the AATCC Gray Scale, the higher the evaluation

75 number, the less is the stain. Table V which follows provides soil redeposition data for untreated and treated (with the agent of the invention) fabrics. The soiling procedure was carried out on fabric samples treated with the agent of the invention and on such 80 samples which had been washed 5X and 10X, that is, washed 5X and 10X after application of the agent before being subjected to the soiling procedure. The agent was applied to the fabric, by the procedure already given, with curing in the presence of sodium sulfate/citric acid being carried out for 1 minute at the temperature indicated in the table.

TABLE V

	<i>Agent from Ex. No.</i>	Cure Temp. (°C)	Gray Scale Reading		
			1	5W	10W
5	26*	182	4	3	3
	27**	199	5/4	5/4	5/4
	28**	199	5/4	5/4	5/4
10	Untreated fabric* (Control)	—	3	1	1
	Untreated fabric** (Control)	—	2	2	2

*white Qiana®

**polyester

Experiments 1 to 5

The following Experiments 1 to 5 are intended to show various compositions which fail to meet the aforesaid requirements of the invention and which, therefore, are outside the invention. Data summariz-

ing Experiments 1 to 5 are given in Table VI. The definitions of formula terms and code designations are the same as given above for Examples 1 to 45 (in all cases, X is the same as in said examples, excluding Example 44).

TABLE VI

	<i>Expt. No.</i>	<i>(a)</i>	<i>Y₁</i>	<i>(b)</i>	<i>Y₂</i>	<i>(c)</i>	<i>Y₃</i>	Viscosity (pascal seconds)		
								<i>HLB</i>	<i>S.R.</i>	<i>5W</i>
30	1	0	—	0	—	1	G ₃	16.8	0.025	
	2	1	A ₁	1.2	A ₂	1	A ₃	16.1	0.236	
	3	1	A ₁	1.2	A ₂	1	A ₃	16.1	0.082	
35	4	1	A ₁	1	C ₂	1	M ₃	18.1	1.570	
	5	1	A ₁	1	F ₂	1	C ₃	18.2	3.700	
	<i>Expt. No.</i>			<i>A.S.</i>				<i>10W</i>	<i>5W</i>	<i>10W</i>
40	1	12.86	14.08	14.43	1	—	—			
	2	12.77	15.25	15.73	4	4	3			
	3	12.41	13.88	14.50	4	2	2			
	4	12.41	13.61	14.47	3	3	—			
	5	12.50	13.95	14.96	3	3	2			

BEST MODE FOR CARRYING OUT THE INVENTION

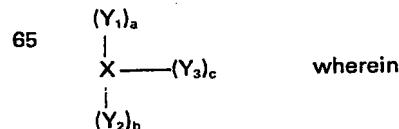
The best mode for carrying out the invention resides in the embodiments described above wherein the agent of Example 26 is applied by pad application to 6 ounce (0.170 kg) doubleknit fabric of 100% polyester filament, using calcium nitrate in the pad bath, with curing of the agent on the fabric being effected in 0.75 minute at 199°C.

INDUSTRIAL APPLICABILITY

55 The invention disclosed herein is particularly useful for imparting durable, antistatic, soil release characteristics to textile fabric treated with the agent of the invention by the process of the invention.

CLAIMS

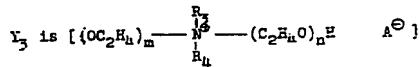
60 1. Process for applying durable, antistatic soil release agent to a substrate, said agent being of the formula



70 X is an aminoplast resin moiety having amino nit-

rogen atoms and 4 to 6 methylene groups, each of which methylene groups is attached to an amino nitrogen atom and to Y₁, Y₂ or Y₃;

75 Y₁ is O(C₂H₄O)₅₋₂₀R₁ wherein R₁ is C₁₋₅ alkyl; Y₂ is O(C₂H₄O)₅₋₈₀R₂ wherein R₂ is C₆₋₂₀ alkyl;



80 wherein R₃ is C₄₋₂₀ alkyl, C₄₋₂₀ alkenyl or benzyl, R₄ is C₁₋₄ alkyl, A[⊖] is an organic or inorganic anion, each of m and n is at least 1 and the sum of m and n is 12 to 100;

each of a and b is 0 to 2 and the sum of a and b is

85 0 to 2;

c is 1 to 2;

the sum of a, b and c is 1 to 4;

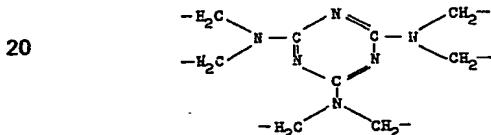
said agent having a calculated hydrophile - lipophile balance (HLB) of 14.5 to 18.0, a 20 weight % aqueous

90 solution viscosity, as measured at 20°C on a Brookfield viscometer, of 0.250 to 16,000 pascal seconds, an electrical resistivity (Keithley log R) on polyester fabric, at 20 ± 2% relative humidity and 23 ± 1°C, of no greater than 13.00 initially and no greater than 14.25 after ten washes, and a soil release rating on polyester fabric of at least 3 initially, said process

- comprising the steps:
- diluting the agent with a normally liquid medium to achieve the desired application liquid viscosity,
 - (b) adding sufficient salt of a mono-, di- or trivalent metal or of an ammonium cation to achieve a cloud point (measured as described herein), of the diluted agent of step (a), of less than 100°C but greater than 25°C, or adding sufficient polyacidic compound having a second dissociation constant of greater than 1×10^{-8} to achieve a pH of the diluted agent of step (a) of 3.0 to 6.0, or adding both said salt and said polyacidic compound to achieve said cloud point and pH,
 - (c) applying the diluted agent of step (b) to the substrate to be treated so as to achieve the desired level of agent on the substrate,
 - (d) drying and curing the agent on the substrate, and
 - (e) recovering substrate which has been durably treated with the agent of the aforesaid formula.
2. Process as claimed in Claim 1 wherein the normally liquid medium is water.
3. Process as claimed in Claim 1 or Claim 2 wherein step (b) is carried out by adding only salt and step (c) is an exhaust application step.
4. Process as claimed in Claim 1 or Claim 2 wherein step (b) is carried out by adding only polyacidic compound and step (c) is a pad application step.
5. Process as claimed in Claim 1 or Claim 2 wherein step (b) is carried out by adding salt and polyacidic compound and step (c) is a pad application step.
6. Process as claimed in any of the preceding claims wherein the substrate is a textile fiber.
7. Process as claimed in Claim 6 wherein the substrate is a textile fabric.
8. Process as claimed in Claim 7 wherein the substrate is a polyester textile fabric.
9. Process as claimed in Claim 7 wherein the substrate is a polyamide textile fabric.
10. Process as claimed in Claim 2 wherein the agent in step (a) is diluted as to provide a ≥ 20 weight % aqueous solution of agent.
11. Process as claimed in Claim 10 wherein the substrate is a textile fabric and curing in step (d) is carried out at 149 to 204°C.
12. Process as claimed in Claim 11 wherein the substrate is a polyester textile fabric and curing in step (d) is carried out in 0.25 to 6 minutes.
13. Process as claimed in any one of the preceding claims wherein curing is carried out at 193 to 199°C for 0.25 to 1.25 minutes.
14. Process as claimed in any one of the preceding claims wherein the salt is the nitrate, phosphate, chloride, sulfate, oxalate, acetate or citrate of a sodium, magnesium, calcium, zinc, aluminum or ammonium cation.
15. Process as claimed in any one of Claims 1 to 13 wherein the salt is calcium nitrate.
16. Process as claimed in any one of the preceding claims wherein the polyacidic compound is phosphoric, citric, oxalic, tartaric, succinic, glutaric or polyacrylic acid.
17. Process as claimed in Claim 16 wherein the polyacidic compound is polyacrylic acid having a molecular weight of up to about 5,000.
18. Process as claimed in any one of claims 1 to 13 wherein the salt is sodium sulfate and the polyacidic compound is citric acid.
19. Process as claimed in any one of Claims 1 to 13 wherein the salt is calcium nitrate and the polyacidic compound is citric acid.
20. Process as claimed in any one of the preceding claims wherein Y_1 is $O(C_2H_4O)_{10-16}$ and R_1 is CH_3 , wherein Y_2 is $O(C_2H_4O)_{15-30}$ and R_2 is $C_{13}H_{27}$, wherein R_3 is C_{8-18} alkyl, R_4 is CH_3 , A^\ominus is OSO_3CH_3 and $m+n$ is 20 to 50, and wherein X is
-
21. Process as claimed in any one of the preceding claims wherein the HLB is 15.5 to 17.0 and the viscosity is 2,000 to 8,000 pascal seconds.
22. Process as claimed in any one of Claims 1 to 19 wherein a is greater than 0 in the first general formula set forth in Claim 1.
23. Process as claimed in any one of Claims 1 to 19 or 22 wherein b is greater than 0 in the first general formula set forth in Claim 1.
24. Process as claimed in Claim 23 wherein each of a and b is greater than 0.
25. Process as claimed in any one of the preceding claims wherein the pH in step (b) is 4.0 to 5.5.
26. Process for applying durable, antistatic soil release agent to a substrate substantially as described herein with reference to the Examples.
27. Substrates, including textile fibers and fabrics, whenever treated by the process claimed in any one of the preceding claims.
28. A durable, antistatic soil release agent which is resistant to yellowing on the substrate treated therewith and which is of the formula
- $$\begin{array}{c} (Y_1)_a \\ | \\ X-(Y_3)_c \\ | \\ (Y_2)_b \end{array} \quad \text{wherein}$$
- X is an aminoplast resin moiety having amino nitrogen atoms and 4 to 6 methylene groups, each of which methylene groups is attached to an amino nitrogen atom and to Y_1 , Y_2 or Y_3 ;
- 120 Y_1 is $O(C_2H_4O)_{5-20}R_1$ wherein R_1 is C_{1-5} alkyl; Y_2 is $O(C_2H_4O)_{5-20}R_2$ wherein R_2 is C_{6-20} alkyl;
- $$X_3 \text{ is } [(\text{ac}_2\text{H}_1)_m-\overset{\overset{R_3}{|}}{\text{N}}^{\ominus}-\text{(C}_2\text{H}_4\text{O})_n]^{\ominus} \quad A^\ominus$$
- 125 wherein R_3 is C_{4-20} alkyl, C_{4-20} alkenyl or benzyl, R_4 is C_{1-4} alkyl, A^\ominus is an organic or inorganic anion, each of m and n is at least 1 and the sum of m and n is 12 to 100;
- 130 each of a and b is 0 to 2 and the sum of a and b is 0

to 2;
c is 1 to 2;
the sum of a, b and c is 1 to 4;
said agent having a calculated hydrophilic - lipophile balance (HLB) of 14.5 to 18.0, a 20 weight% aqueous solution viscosity, as measured at 20°C on a Brookfield viscometer, of 0.250 to 16.000 pascal seconds, and electrical resistivity (Keithley log R) on polyester fabric, at 20 ± 2% relative humidity and 23 ± 1°C, of no greater than 13.00 initially and no greater than 14.25 after ten washes, and a soil release rating on polyester fabric of at least 3 initially.

29. An agent as claimed in Claim 28 wherein Y₁ is O(C₂H₄O)₁₀₋₁₆ and R₁ is CH₃, wherein Y₂ is O(C₂H₄O)₁₅₋₃₀ and R₂ is C₁₃H₂₇, wherein R₃ is C₆₋₁₈ alkyl, R₄ is CH₃, A[⊖] is OSO₃CH₃ and m + n is 20 to 50, and wherein X is



25 30. An agent as claimed in Claim 28 wherein a is greater than 0.
31. An agent as claimed in Claim 28 wherein b is greater than 0.
32. An agent as claimed in Claim 28 wherein each of a and b is greater than 0.
33. An agent as claimed in any one of Claims 28 to 32 wherein HLB is 15.5 to 17.0 and the viscosity is 2.000 to 8.000 pascal seconds.
34. An agent as claimed in any one of Claims 28 to 33 dispersed or dissolved in a normally liquid medium.
35. An agent as claimed in Claim 34 wherein the normally liquid medium is water.
36. An agent as claimed in Claim 35 dissolved in water to form a ≈20 weight % aqueous solution.
37. An agent as claimed in Claims 35 or 36 wherein the aqueous solution includes a salt of a mono-, di or trivalent metal or of an ammonium cation.
45 38. An agent as claimed in Claim 37 wherein the salt is the nitrate, phosphate, chloride, sulfate, oxalate, acetate or citrate of a sodium, magnesium, calcium, zinc, aluminum or an ammonium cation.
39. An agent as claimed in any one of Claims 35 to 38 wherein the aqueous solution includes a polyacidic compound having a second dissociation constant greater than 1 × 10⁻⁸.
40. An agent as claimed in Claim 39 wherein the polyacidic compound is phosphoric, citric, oxalic, tartaric, succinic, glutaric or polyacrylic acid.
55 41. An agent as claimed in Claim 43 wherein the polyacidic compound is polyacrylic acid having a molecular weight of up to about 5,000.
42. An agent as claimed in Claim 35 wherein the aqueous solution includes sodium sulfate and citric acid.
43. An agent as claimed in Claim 35 wherein the aqueous solution includes calcium nitrate and citric acid.
65 44. A substrate which has been treated with an

antistatic soil release agent claimed in any of Claims 28 to 43.

45. A substrate as claimed in Claim 44 which is a polyester textile fabric.
70 46. A substrate as claimed in Claim 44 which is a polyamide textile fabric.

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